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"A luminescence Study of mixed ligand complexes of Thorium (IV) with Oxygen, Sulfurand nitrogen donor ligands; as possible precursor for luminescence material"

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ABSTRACTS: The mixed ligand Complexes of Th(IV) with substituted pyrazolines and dithophosphoric acid ligands of the type $[Th(S_2PO_2R)_2(C_{15}H_{12}N_2OX)_2].nH_2O$ (where X= H, OCH_3, CH_3, Cl and (R= $CH_2C(CH_3)$ CH_2-, $CH_2CH_2CH(CH_3)$-) have been synthesized and characterized by elemental analysis, molecular weight, IR, TGA, SEM,XRD and U.V. visible spectral measurements. The fluorescent property of these synthesized mixed ligand complexes have been studied by fluorescence spectrophotometer. It's different from others freshly published on thorium due to its high luminescence property with nano size applications.

Key words: Thorium, Pyrazolone, Dithiophosphate, Luminescence.

1. INTRODUCTION

Thorium is the most common radioactive element in nature [1, 2]. Its chemistry presents an excellent area of research, because of its possibility of formation of compounds with high coordination number, a few of them observed in transition metal chemistry [3]. Thorium (IV) shows High charge along with its effective ionic size and due to this the metal enables to form complexes with high coordination number [4, 5].The metal shows a large number of tetrahedral, octahedral, and dodecahedral geometry are known [7, 8]. The Actinides are always being the key of interest for the nuclear industry and extraction and analytical applications [9-11]. The actinide is not only one of the heaviest metals but it has not left any valence electrons in there valence shell and due to this it's hardly oxidizing. Thorium (IV) complexes have the excellent feature for the observation of Intra ligand phosphorescence at room temperature [12]. Pyrazolines are an important class of heterocyclic compounds. It has many applications in the field of industries as dyes, antioxidant in lubricating oils [13] in agriculture as catalyst and also commonly used as inhibitor for plant growth [14-16]. The Organic derivatives of the pyrazolines are commonly used in photography [17] and the derivatives act as patent antibacterial & antifungal agents [18]. However dithiophosphoric acids of lanthanide and actinides crate some ataintation for the researcher [10-12]. The present paper reports the synthesis, characterization, luminescence behavior and the nano material properties of mixed ligand complexes of thorium (IV) complexes with sulfur nitrogen and oxygen donor ligands. The mixed ligand complexes are prepared by the reaction of metal, pyrazolines and dithiophosphoric acid as a ligand.

2. EXPERIMENTAL

Analytical grade of thorium (IV) nitrate hexahydrate was used as such without further purification. Solvents like isopropanol, ethanol and benzene were rigorously dried and purified and laboratory grade chemicals whenever used were distilled and purified according to standard procedures [19]. 3(2-Hydroxyphenyl)-5-(4-substituted phenyl) pyrazolines were prepared by reported procedure [20, 21]. While the Ammonium salt of O' O –dialky and alkylenedithiophosphoric acid was prepared by the reaction of phosphorus petnasulphides (Dry alcohol or glycol). Respectively, in dry benzene followed by the passing ammonia into the solution [22]

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2.1. Synthesis of $[Th(S_2PO_2R)_2 (C_{15}H_{12}N_2OX)_2].H_2O$

The mixed ligand complexes of Thorium (IV) with general formula $[Th(S_2PO_2R)_2(C_{15}H_{12}N_2OX)_2].H_2O$ were prepared by the following reaction path in following two step

Step-I

In the first step the metal nitrate reacts with the ligand pyrazoline into 1:2molar ration and form metal pyrazoline complex. In this process nitrate separated in the form of sodium nitrate.

$$[Th(NO_3)_4].nH_2O + 2Na[(C_{15}H_{12}N_2OX)_2] \rightarrow [Th(NO_3)_2 (C_{15}H_{12}N_2OX)_2.nH_2O] + 2Na(NO_3)$$

Step-II

In the second step the the metal pyrazoline reacts with the ammonium salt of dithiophosphoric acid and form the final metal ligand complex. The reaction performs in 1:2 molar rations with the metal. All the type of metal mixed ligand complexes form with the same reaction procedure.

$$[Th(NO_3)_2 (C_{15}H_{12}N_2OX)_2.nH_2O] + 2 [NH_4[S_2PO_2R] \rightarrow [Th (C_{15}H_{12}N_2OX)_2(S_2PO_2R)_2.H_2O] + 2NH_4(NO_3)$$

Where **X =** H, Cl, CH_3, OCH_3, **R =** $(CH_2C(CH_3)_2CH_2$ and for other complex **n=**1,2,3,….

2.2. Synthesis of $[Th(S_2PO_2R')_2 (C_{15}H_{12}N_2OX)_2].H_2O$

The mixed ligand complexes of Thorium (IV) with general formula $[Th(S_2PO_2R')_2(C_{15}H_{12}N_2OX)_2].H_2O$ were prepared by the following reaction path in following two step

Step-I

In the first step the metal nitrate reacts with the ligand pyrazoline into 1:2molar ration and form metal pyrazoline complex. In this process nitrate separated in the form of sodium nitrate.

$$[Th(NO_3)_4.nH_2O] + 2Na(C_{15}H_{12}N_2OX)_2[Th(NO_3)_2 \rightarrow (C_{15}H_{12}N_2OX)_2.nH_2O] + 2Na(NO_3)$$

Step-II

In the second step the metal pyrazoline reacts with the ammonium salt of dithiophosphoric acid and form the final metal ligand complex. The reaction performs in 1:2 molar rations with the metal. All the type of metal mixed ligand complexes form with the same reaction procedure.

$$[Th(NO_3)_2 (C_{15}H_{12}N_2OX)_2.H_2O] + 2 [NH_4[S_2PO_2R] \rightarrow [Th (C_{15}H_{12}N_2OX)_2 (S_2PO_2R)_2.H_2O] + 2NH_4(NO_3)$$

Where **X =** H, Cl,CH_3, OCH_3, **R'** =$(CH_2CH_2CH(CH_3)$ and **n =** 1,2,3,….

3. INSTRUMENTATION

Chlorine was estimated by volumetric Volhard's method [22]. For the determination of molecular weights, the molecular ion peak is detected by DART mass spectra on a JMS-T100LC Accu TOF mass spectrometer. Elemental analysis (C, H, N, S and O) were carried out on Elementar Vario EL III analyzer. Thorium was estimated by decomposing the compound by boiling with HNO_3 till dryness. This process was repeated 4-5 times then solid was treated with water followed by oxalic acid solution. The precipitate was filtered. Washed and then ignite in platinum crucible and weight as ThO_2 [23]. Electronic spectra were recorded in Chloroform solution on Varian, Cary 5000 UV-visible spectrophotometer within 5 x to 300,000 x (Both High and Low Vacuum Models). X-ray diffraction studies were carried out on model Bruker AXS D8 Advance diffractometer at temperature range -170 °C to +450 °C. Thermo gravimetric analysis for the compounds has been carried out by using Perkin Elmer TGA. Luminescence studies have been done by Double Beam Spectrophotometer U-2900/2910 in the range 190 to 1100 nm range. Life time system was carried out on fluorocube.

4. RESULTS AND DISCUSSION

Complexes of type $[Th(C_{15}H_{12}N_2OH)_2 \{(S_2PO_2 (CH_2C(CH_3)_2 CH_2\}_2.H_2O]$ and $Th(C_{15}H_{12}N_2OH)_2 \{(S_2PO_2 (CH_2CH_2 CH (CH_3)\}_2. H_2O]$ are white in color and soluble in common organic solvents such as benzene, toluene, chloroform at room temperature. The molecular weight (DART Mass) data shows the monomeric nature of the complexes. The elemental analysis(C, H, N, O, S, Cl) data are in according with their stereochemistry proposed in given table 1.

4.1. Nuclear Magnetic Resonance (NMR) Spectra

4.1.1. ^{1}H-NMR Spectra

^{1}H NMR spectra (In $CDCl_3$) shows signals in the range 3.68-3.48 ppm as triplet and 2.48-1.92 ppm

Table 1
Physical and Analytical Details of Complexes

S. No.	*Compounds*	*% Yield*	*Decpcom -position point (^0C)*	*Mol. Weight Obs. (Calc.)*	*Elemental Analysis Found Cal. in %*							
					C Obs. (Calc.)	*H Obs. (Calc.)*	*N Obs. (Calc.)*	*O Obs. (Calc.)*	*Cl Obs. (Calc.)*	*S Obs. (Calc.)*	*P Obs. (Calc.)*	*Th Obs. (Calc.)*
1	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ (Amorphous /White)	91	258	1120.11 (1119.08)	42.23 (42.93)	4.01 (4.32)	5.23 (5.01)	11.09 (10.01)	-	11.19 (11.46)	6.07 (5.54)	21.13 (20.73)
2	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ (Amorphous / Pale white)	86	227	1188.03 (1187.97)	40.02 (40.44)	3.98 (3.90)	4.08 (4.72)	9.40 (9.43)	5.91 (5.97)	11.01 (10.80)	5.10 (5.21)	20.04 (19.53)
3	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ (Amorphous / Pinkish white)	83	238	1148.21 (1147.13)	42.02 (43.97)	4.85 (4.57)	4.75 (4.88)	9.80 (9.76)	-	10.94 (11.18)	5.82 (5.40)	21.42 (20.23)
4	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ (Amorphous / Yellowish white)	86	245	1180.02 (1179.13)	43.15 (42.78)	4.84 (4.44)	4.68 (4.75)	12.07 (12.21)	-	11.36 (10.88)	5.51 (5.25)	20.02 (19.68)
5	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$ (Amorphous /Pinkish white)	93	250	1100.17 (1091.02)	41.06 (41.83)	4.42 (4.06)	5.98 (5.14)	10.04 (10.27)	-	12.52 (11.76)	5.48 (5.68)	22.10 (21.27)
6	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$ (Amorphous /White)	80	240	1201.62 (1159.91)	40.08 (39.35)	3.77 (3.65)	4.40 (4.83)	9.49 (9.66)	6.67 (6.11)	12.05 (11.06)	5.81 (5.34)	21.10 (20.00)
7	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$ (Amorphous /Light white)	82	224	1120.03 (1119.08)	42.71 (42.93)	4.38 (4.32)	5.63 (5.01)	11.05 (10.10)	-	12.03 (11.48)	4.93 (5.54)	21.25 (20.73)
8	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$ (Amorphous /White)	86	237	1152.45 (1151.07)	42.03 (41.74)	4.40 (4.20)	4.92 (4.87)	12.82 (12.51)	-	12.21 (11.14)	5.41 (5.38)	21.05 (20.16)

as doublet due to the presence of CH_2 and CH [24] other signal found at the range of 7.92-6.24 ppm as multiplate due to five membered ring [25]. The N-H peak found in the range of 5.46-5.04 ppm as a broad signal [26].Other signal observe at 3.91 and 3.88 ppm for the OCH_3.All the data are given in the table 2.

4.1.2. ^{13}C NMR spectra

The 13CNMR spectra were recorded in $CDCl_3$. The spectra shows signals at 132.01-120.80 ppm due to the aromatic carbon and higher signals observe at 142.02-136.02ppm due to the C=N .The spectra shows a singlet at the region 81.42ppm [27] due to the presence of dithiophosphoric acid. This shows low shifting with respect to metal salt [28]. In alkylenedithiophosphoric acids, [28] the chemical shift seem to be affected by the number of atoms in the heterocyclic ring. Other signals observe in the region of 43.08-42.01ppm and 51.02-50.12 due to the CH_2 carbon of five membered rings and CH [25]. All the data are given in the table 3.

4.2. Thermo gravimetrical analysis

The TG studies show the thermal stability of the complexes. Both the complexes show gradual loss in the weight due to the fragmentation increases as increase the temperature. All the complexes show similar behavior with respect to TG study. Like most of the complexes, the complexes also decompose and obtained in the form of metal oxide i.e. ThO_2.The fragmentation occur of the $-H_2O$, Pyrazoline and dithiophosphate at the different temperature region 171.42 °C, 174.42 °C for water molecule fragmentation which is outside coordination sphere, 410.32 °C and 420.22 °C for the fragmentation of Pyrazoline, 542.31 °C and 552.48 °C for the dithiophosphate fragmentations. The temperature region 580.35 °C and 578.76 °C show that the stability of metal mixed ligand complexes which determines the ThO_2. The constant weight shows the compilation of reaction. The metal oxide was confirmed by the X-ray diffraction pattern of the decompose complex [29].

Table 2
^{1}H-NMR Spectral data of Complexes

Sl. No.	*Complexes*	*Chemical Shift (in ppm)*				
		Ar-H	*-CH_2*	*-NH*	*-CH*	*-OCH_3*
1	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	7.92-7.39	3.68	5.46	2.48	_
2	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	7.89-7.04	3.57	5.39	2.36	_
3	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	7.64-7.53	3.56	5.21	2.34	_
4	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	7.47-7.27	3.54	5.32	2.11	3.91
5	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	7.88-6.24	3.48	5.04	1.92	_
6	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$	7.31-7.09	3.49	5.14	2.28	_
7	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$	7.26-7.18	3.51	5.28	2.38	_
8	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	7.84-6.98	3.58	5.42	2.28	3.88

Table 3
^{13} C-NMR Spectral data of Complexes

Sl. No.	*Complexes*	*Chemical shift (in ppm)*				
		ν (C=N)	*ν (Ar-C)*	*ν (CH)*	*ν (CH_2)*	*ν (OCH_3)*
1	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	142.02	131.01, 125.43	51.02	43.08	-
2	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	138.92	128.82, 127.12	50.46	42.81	-
3	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	139.35	126.71, 128.74	50.31	43.02	-
4	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	140.13	128.61,126.81	50.23	42.18	61.62
5	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	136.02	125.86,120.80	50.12	42.01	-
6	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$	134.37	128.28,129.93	50.89	42.11	-
7	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$	137.83	122.84,123.66	50.82	42.88	-
8	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	138.91	128.08,123.04	50.71	42.39	61.38

4.3. DART Mass spectra

The DART Mass spectral study shows the monomeric nature of both the complexes. The molecular ion peak observed for the $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ and $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$ complexes 1120.11 and 1100.17 other details are listed as the table 4

4.4. UV.-Vis. Spectra

The UV.-Vis. Spectral study shows the metal ligand π- π* and *n*- π* transition and the observed wavelength shifted towards the lower side. This result the synthesized both the complexes shows color. The absorption spectral data of $[Th(C_{15}H_{12}N_2OH)_2\{(S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O$ in chloroform show absorption in the region 36,144-37,120 cm^{-1} can be assigned to intra ligand π- π* and *n*- π* transitions of the pyrazoline [24].The wavelength shifts into the lower side which indicates the π-π* and *n*- π* transition through ligand to metal. Metal dithiophosphate also reports the lower shifting of wavelength. Electronic absorption spectral data of and $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O$ in benzene show absorption in the regions 28,940-30,210 and 38,748-39,311 cm^{-1}. Bands in the region 30,948-31,480 cm^{-1} may be assigned to metal to ligand charge transfer transition and bands in the region 38,578-39,329 cm^{-1} can be assigned to intra ligand, π- π* and *n*- π* transitions of the pyrazoline [25].The other ligand dithiophosphate also shows the lower shifting of wavelength which shows the color of compound. Both the complexes colored in nature.

4.5. XRD and SEM Studies

XRD and SEM study describe the morphology of the complexes both the complexes are amorphous in nature and shows size near to nano which is observed by the XRD images. The Particle size for the complexes$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ and $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$ shows as 2.13 µm and 1.94 ìm with respect to SEM images while the average diameter (XRD) shows 52 nm and 38 nm. The XRD and SEM details listed as table 5.

4.6. Luminescence and Life time study

Both the complexes are luminescence active and show strong luminescence property. The absorption spectra for both the complexes (Sl. No. - 01 and 05) observe at 348 and 349nm, (Figure No. 1 and 3) while the emission spectra shows higher values as 798 and 518 nm as absorption spectra (Figure No.-02 and 04). The discussed complexes shows good % quantum yield as 43 and 66% .On the basis of these analysis and calculation shows that the both the complexes are luminescence active and these show high

Table 4
DART Mass spectral data of the Complexes

Sl. No.	*Complexs*	*Mol.wt. Obs. (calcd.)*	*-H_2O Obs. (calcd)*	*-2Py Obs. (calcd.)*	*-2DTP Obs. (Calcd.)*
1	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	1120.11 (1119.08)	1106.04 (1101.06)	628.25 (626.51)	234.06 (232.02)
2	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	1188.03 (1187.97)	1170.65 (1169.95)	628.65 (626.51)	231.85 (232.04)
3	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	1148.21 (1147.13)	1132.04 (1129.11)	628.32 (626.95)	234.28 (232.48)
4	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	1180.02 (1179.13)	1162.64 (1161.11)	628.32 (626.51)	228.63 (227.04)
5	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	1100.17 (1091.02)	1074.02 (1073)	600.12 (598.45)	234.68 (232.03)
6	$[Th(C_{15}H_{12}N_2OCl)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$	1201.62 (1159.91)	1142.21 (1141.89)	601.44 (598.45)	234.54 (232.03)
7	$[Th(C_{15}H_{12}N_2OCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O\ ]$	1120.03 (1119.08)	1104.22 (1101.06)	604.01 (598.45)	231.90 (232.03)
8	$[Th(C_{15}H_{12}N_2OOCH_3)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	1152.45 (1151.07)	1135.44 (1133.05)	600.40 (598.45)	234.50 (232.03)

luminescence properties[26].The lifetime study of complexes show that these are fluorescence as they shows there life time in nano second. The life time details of both the complexes given as the table 6.

Table 5
XRD and SEM of the complexes

Sl No.	*Complexes*	*Average diameter (by XRD) nm*	*Average diameter (by SEM) um*
1	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	52.31	2.13
5	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	38.14	1.94

Table 6
Luminescence and life time analysis of the complexes

Sl no.	*Complexes*	*Absorption (nm)*	*Emission (nm)*	*Φ*	*τ(nsec)*
1	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$	**348**	**798**	**0.43**	**32.01**
5	$[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.H_2O]$	**349**	**522**	**0.66**	**30.22**

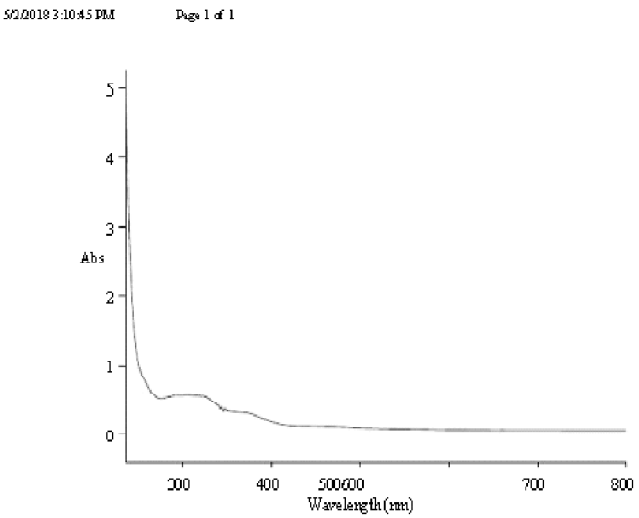

Figure 1: Absorption spectrum of $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ Complex

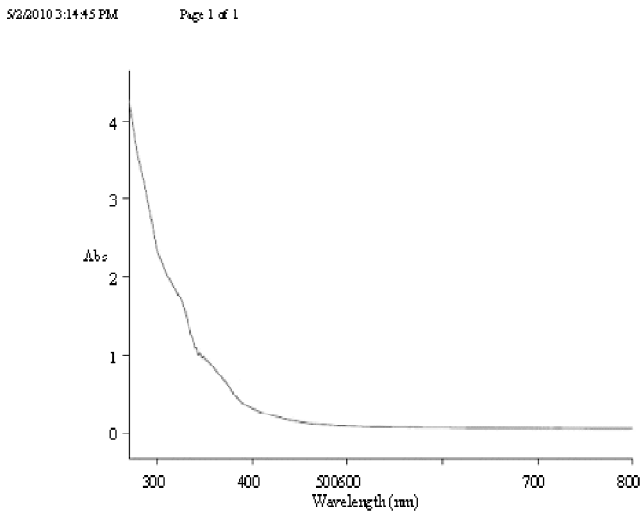

Figure 3: Absorption spectrum of $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ Complex

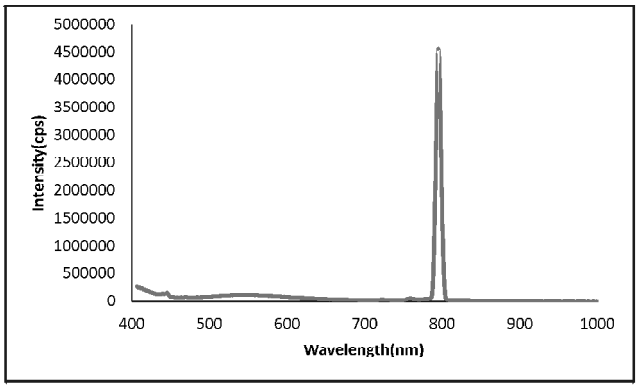

Figure 2: Emission spectrum of $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.nH_2O]$ Complex

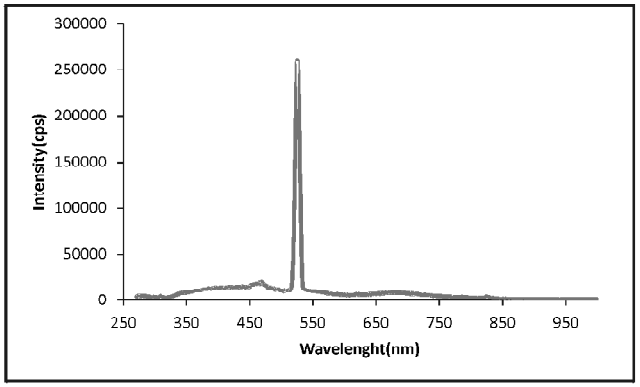

Figure 4: Emission spectrum of $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.nH_2O]$ Complex

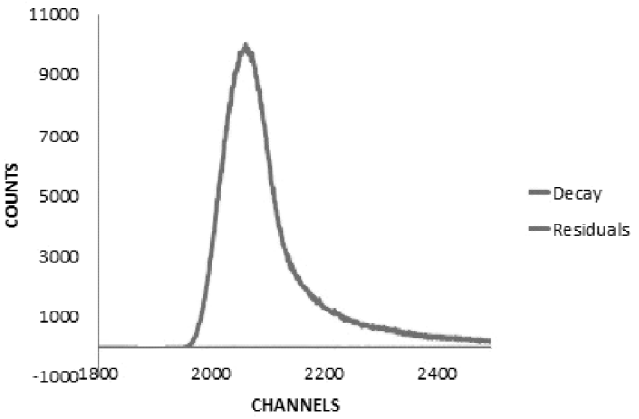

Figure 5: Life Time image of $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ Complex

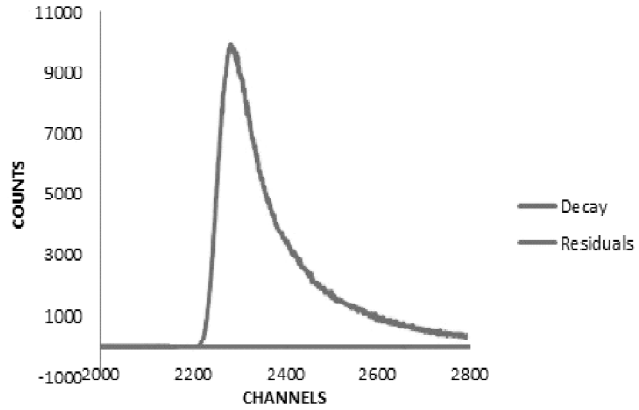

Figure 6: Life Time image of $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.nH_2O]$ Complex

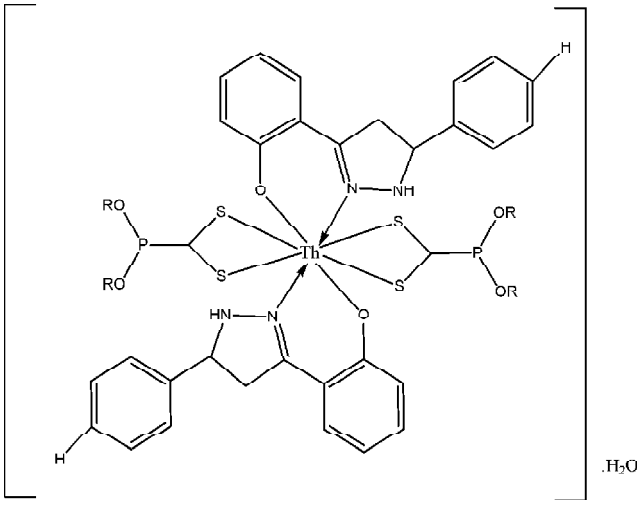

Figure 7: Structure of the $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2C(CH_3)_2CH_2\}_2.H_2O]$ Complex

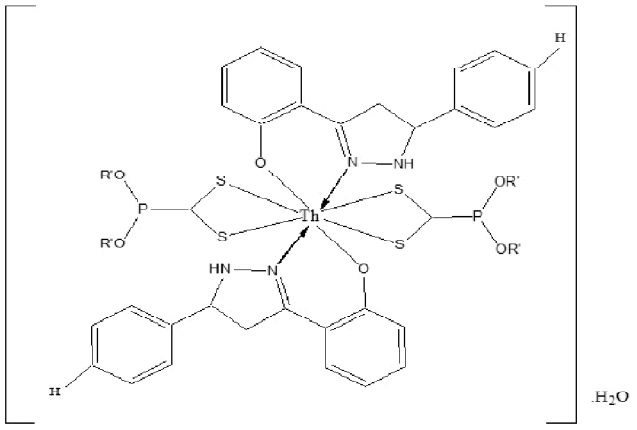

Figure 8: Structure of the $[Th(C_{15}H_{12}N_2OH)_2\{S_2PO_2(CH_2CH_2CH(CH_3)\}_2.nH_2O]$ Complex

5. CONCLUSIONS

On the basis of the above discussion and calculated data on the Thorium mixed ligand complexes following conclusion may be drawn The DART mass spectra shows the monomeric nature of the complexes. U. V. vis. spectra shows the metal ligand transition and color properties. XRD and SEM images show the amorphous nature and there nano particle size. TGA analysis shows the fragmentation pattern for water molecule, both ligands (Pyrazoline and ditiophosphate) and metal oxide. The Luminescence study support the luminescence is a type of fluorescence, life time study show excited state stability of electrons and the % quantum yield shows that the high % of luminescence activity of the complexes, Putting all the fact together both the complexes shows the geometry around the Th(IV) metal is dodecahedral with Coordination No. 08(Figure No. 07 and 08).

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